Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A non-centrosymmetric one-dimensional coordination polymer: *catena*[[(4,7-phenanthrolin-4-ium-κN^7)(thiocyanato-κS)copper(I)]-μ-thiocyanato-$\kappa^2 N$:S]

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The title compound, $[Cu(NCS)_2(C_{12}H_9N_2)]_n$, is a one-dimensional coordination polymer containing tetrahedrally coordinated Cu^I atoms bound to one N atom from a protonated 4,7-phenanthroline ligand, and one N and two S atoms from three distinct thiocyanate anions. In the crystal structure, chain motifs align parallel to the *a* axis, formed from the linkage of neighboring Cu^I atoms through bridging thiocyanate ligands.

Received 11 December 2006
Accepted 13 December 2006

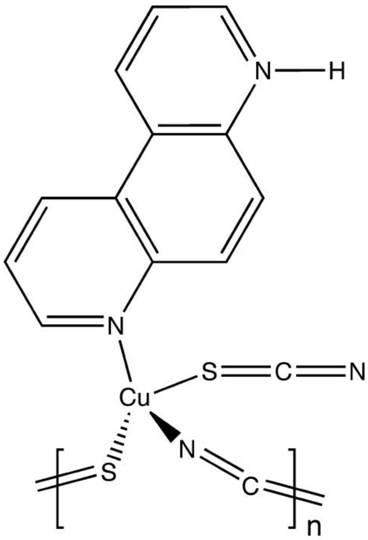
Key indicators

Single-crystal X-ray study
T = 94 K
Mean σ(C–C) = 0.004 Å
R factor = 0.033
wR factor = 0.064
Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Non-centrosymmetric coordination polymers have been recently investigated successfully as non-linear optical (NLO) materials for second harmonic generation (Evans & Lin, 2002). Several reports have shown the utility of copper(I) thiocyanate as a versatile building block for the construction of inorganic/organic hybrid solids, with chain, staircase, layer and network morphologies accessible through judicious choice of organic component (Blake *et al.*, 1999).



(I)

In an attempt to prepare NLO-active copper(I) thiocyanate coordination polymers, the title compound, (I), was prepared *via* hydrothermal self-assembly. Compound (I) crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$, and its structure is based on $[Cu^IN_2S_2]$ distorted coordination tetrahedra (Fig. 1). Selected bond lengths and angles are given in Table 1. The two S donors belong to two distinct thiocyanate ligands, one of which serves as a monodentate ligand while the other acts as a bridge to another neighboring Cu^I atom. One of the N donors belongs to another bridging thiocyanate ligand, with the fourth coordination site occupied by an N atom

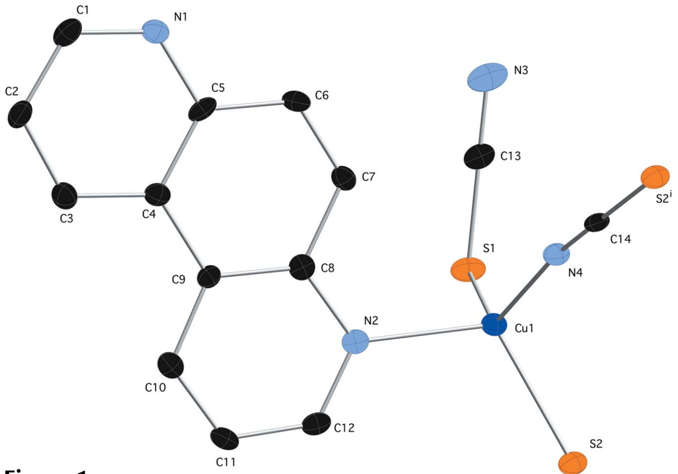


Figure 1
The asymmetric unit of the title compound, with symmetry-equivalent S atom to complete the bridging thiocyanate ligand, showing 50% probability ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. The symmetry code is as in Table 1.

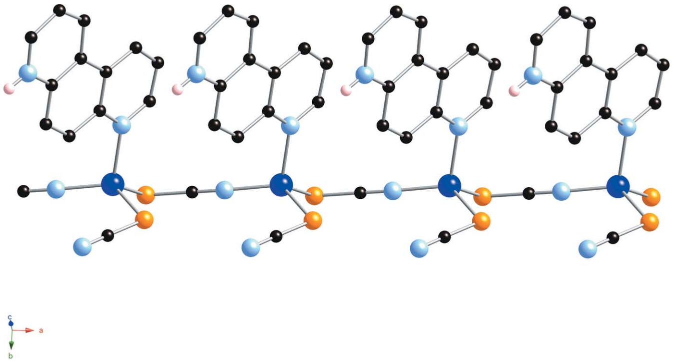


Figure 2
A single polymeric one-dimensional chain motif, which lies parallel to the *a* crystal axis. H atoms bonded to C atoms are not shown. Color codes: dark-blue Cu, light-blue N, orange S, black C, pink H.

belonging to a protonated monodentate *4H*-4,7-phenanthroline ligand.

By means of the bridging thiocyanate ligands, one-dimensional $[CuSCN]_n$ chains are formed, which extend parallel to the *a* axis (Fig. 2). The Cu$\cdots$Cu distance along the chain is 5.666 (3) Å, the *a* lattice parameter. Neighboring chains, related by 2_1 screw axes parallel to *a*, aggregate into pseudo-two-dimensional slabs coincident with (011) planes (Fig. 3) *via* N—H$\cdots$N hydrogen bonding (Table 2) between pendant *4H*-4,7-phenanthroline ligands and monodentate thiocyanate N atoms. Adjacent slabs stack along the *c* crystal axis into a three-dimensional structure (Fig.4), formed by van der Waals and crystal packing forces.

Experimental

All chemicals were obtained commercially. A mixture of copper(II) chloride dihydrate (57 mg, 0.33 mmol), sodium thiocyanate (135 mg, 1.66 mmol), 4,7-phenanthroline (60 mg, 0.33 mmol), aqueous hydrochloric acid (0.22 ml,1.0 *M*, 0.22 mmol) and water (6.0 g, 330 mmol) was flame-sealed into a borosilicate glass tube, which was then heated under autogenous pressure at 393 K for 72 h. Red blocks (84 mg, 70% yield based on Cu) of the title compound were obtained after filtration, washing with water and acetone, and drying in air.

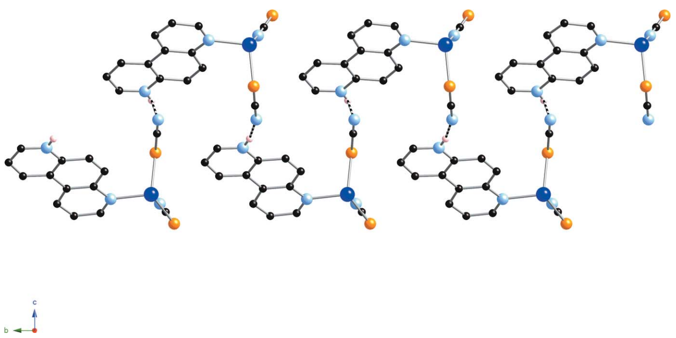


Figure 3
Part of the crystal structure of (I) illustrating the supramolecular aggregation of chain motifs into slabs that lie parallel to the *bc* crystal plane. Hydrogen bonding is shown as dashed lines and only H atoms involved in hydrogen bonding are shown.

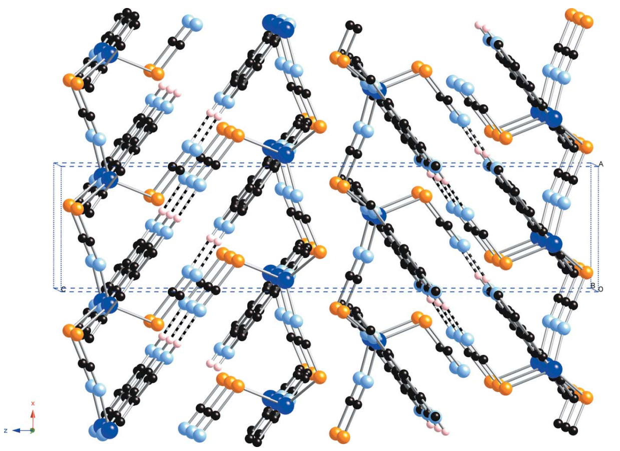


Figure 4
Partial packing diagram illustrating the stacking of two-dimensional slabs to form the three-dimensional structure.

Crystal data

$[Cu(NCS)_2(C_{12}H_9N_2)]$
$M_r = 360.91$
Orthorhombic, $P2_12_12_1$
$a = 5.6662$ (3) Å
$b = 10.1801$ (6) Å
$c = 24.2927$ (15) Å
$V = 1401.26$ (14) Å^3

$Z = 4$
$D_x = 1.711$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.85$ mm^{-1}
$T = 94$ (2) K
Block, red
0.50 × 0.40 × 0.30 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.450$, $T_{\max} = 0.574$

9353 measured reflections
3348 independent reflections
2979 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.064$
$S = 1.06$
3348 reflections
193 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.6847P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Absolute structure: Flack (1983), 1346 Friedel pairs
Flack parameter: 0.031 (13)

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Table 1
Selected geometric parameters (Å, °).

Cu1—N4	1.954 (2)	Cu1—S2	2.3298 (8)
Cu1—N2	2.134 (2)	Cu1—S1	2.3449 (9)
N4—Cu1—N2	107.20 (9)	S2—Cu1—S1	109.96 (3)
N4—Cu1—S2	104.70 (7)	C14—S1—Cu1	105.43 (10)
N2—Cu1—S2	112.11 (7)	C13$^{\rm i}$—S2—Cu1	97.12 (10)
N4—Cu1—S1	123.80 (8)	N3—C14—S1	179.1 (3)
N2—Cu1—S1	99.01 (7)	N4—C13—S2$^{\rm ii}$	179.6 (3)

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$N3$^{\rm iii}$	0.882 (18)	1.84 (2)	2.710 (2)	167.0 (2)

Symmetry code: (iii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

All H atoms bound to C atoms were placed in calculated positions, with C—H = 0.93 Å and refined in riding mode with $U_{\rm iso} = 1.2U_{\rm eq}$(C). The H atom bound to the N atom of the 4*H*-4,7-phenanthroline ligand was found *via* Fourier difference map, restrained with N—H = 0.89 (2) Å and refined isotropically.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Crystal Maker* (Crystal Maker, 2005); software used to prepare material for publication: *SHELXS97*.

We gratefully acknowledge the donors of the American Chemical Society Petroleum Research Fund (Type B Grant for undergraduate research) and Michigan State University for funding this work. The Bruker P4 CCD diffractometer at Syracuse University was purchased with a grant from the National Science Foundation.

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